



Influence of excitons interaction with charge carriers on photovoltaic parameters in organic solar cells

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ABSTRACT

We report on theoretical analysis of excitons annihilation on charge carriers in organic solar cells. Numerical calculations based on transient one-dimensional drift-diffusion model have been carried out. An impact of three quantities (an annihilation rate constant, an exciton mobility and a recombination reduction factor) on current density and concentrations of charge carriers and excitons is investigated. Finally, we discuss the influence of excitons interaction with electrons and holes on four photovoltaic parameters (a short-circuit current, an open-circuit voltage, a fill factor and a power conversion efficiency). The conclusion is that the annihilation process visibly decreases the efficiency of organic photo-cells, if the annihilation rate constant is greater than $10^{-15} \text{ m}^3 \text{ s}^{-1}$.

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1. Introduction

Currently, a great progress in the areas of molecular electronics and organic photovoltaics is observed. Nevertheless, devices based on inorganic materials are still more popular due to their better stability and efficiency. In order to obtain more efficient organic solar cells, it is important to solve a problem which physical processes significantly influence photovoltaic parameters, such as a short-circuit current (J_{sc}), an open-circuit voltage (V_{oc}), a fill factor (FF) and a power conversion efficiency (PCE). In contrast to inorganic photocells, the role of excitons is greater for organic structures [1,2]. For example, a photogeneration of charge carriers occurs as a consequence of excitons dissociation into separated electrons and holes. It seems that also other excitonic processes should give a visible contribution to photoelectric properties of such systems. Therefore, systematical studies of all excitonic effects are of great importance to obtain organic solar cells with higher efficiency.

One of the processes which can occur in molecular systems is the annihilation of excitons on charge carriers [3,4]. Considering a simple scheme of this phenomenon, an electron (a hole), which is a part of an exciton, interacts with a separated hole (electron). As a consequence, both interacting opposite sign charge carriers annihilate and a hole (an electron) from the interacting exciton becomes a free carrier. An alternative interpretation of this process

takes into account a total energy transfer from an exciton to a separated charge carrier. As a result, the exciton is fully quenched. For both scenarios of this effect, a concentration of excitons decreases but concentrations of free electrons and holes are still the same. Recently, the annihilation of excitons on charge carriers has been intensively studied in organic light-emitting diodes [5–11], organic solar cells [12–20] and organic light-emitting transistors [21]. It is believed that this process should give a significant contribution to the loss of efficiency of these organic optoelectronic devices, especially for high excitation densities [15,22].

The aim of this paper is to investigate an influence of the excitons annihilation on photovoltaic parameters (J_{sc} , V_{oc} , FF and PCE) of organic solar cells under AM 1.5G irradiation which simulates a Sun light in laboratories. In order to achieve this goal, we decided to implement the annihilation process into the one-dimensional transient drift-diffusion model. As to our knowledge [23], the terms concerning the excitons annihilation on charge carriers have not been incorporated to time-dependent drift-diffusion equations by other researchers.

2. Model

First, it should be mentioned about several assumptions used in the presented model. Similarly to earlier numerical studies [24–30], we treat the recombination of charge carriers as a bimolecular process. For simplicity, thermionic and excitonic injection currents from electrodes are not taken into account. In general, the intensity of light decreases exponentially due to absorption. This effect causes that most of light is absorbed near illuminated surface.

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Thus, it is convenient to assume that an illumination is uniform in the whole volume of a very thin sample what leads to a constant value of an exciton generation rate. In addition, we have decided to neglect the exciton-exciton interaction.

Excitons can interact with trapped and free (predominantly slow) charge carriers. Both these mechanisms are characterized by different rate constants. It has been experimentally demonstrated that an annihilation rate constant for the exciton-trapped charge carrier interaction can be even three orders of magnitudes lower than an annihilation rate constant which describes the exciton-free carrier interaction in the same material (anthracene) [31]. Therefore we decided to ignore trapping and detrapping effects in our calculations.

Continuity equations for excitons, electrons and holes are given by relations

$$\frac{\partial S}{\partial t} = G + \frac{1}{4}R_B - \frac{S}{\tau_s} - k_{diss}(E)S - \gamma_{ns}nS - \gamma_{ps}pS - \frac{1}{q} \frac{\partial J_s}{\partial x}, \quad (1)$$

$$\frac{\partial n}{\partial t} = k_{diss}(E)S - R_B + \frac{1}{q} \frac{\partial J_n}{\partial x} \quad (2)$$

and

$$\frac{\partial p}{\partial t} = k_{diss}(E)S - R_B - \frac{1}{q} \frac{\partial J_p}{\partial x}, \quad (3)$$

respectively, where S is a concentration of excitons, n and p are concentrations of electrons and holes, respectively, q is an elementary charge, G represents an exciton generation rate, τ_s is a lifetime of excitons, $k_{diss}(E)$ is an electric field dependent exciton dissociation rate, γ_{ns} and γ_{ps} are the second order rate constants for the annihilation of excitons on electrons and holes, respectively, and R_B is a bimolecular recombination rate for electrons and holes. A term with a factor $1/4$ in Eq. (1) is a consequence of an assumption that 25% of recombining electrons and holes form excitons [26]. It should be noted that terms with the rate constants γ_{ns} and γ_{ps} are not included in Eqs. (2) and (3) because the concentrations of free charge carriers do not change in the process of excitons annihilation.

Current densities of excitons (J_s), electrons (J_n) and holes (J_p) are given by

$$J_s = -\mu_s k_B T \frac{\partial S}{\partial x}, \quad (4)$$

$$J_n = -qn\mu_n \frac{\partial \phi}{\partial x} + \mu_n k_B T \frac{\partial n}{\partial x} \quad (5)$$

and

$$J_p = -qp\mu_p \frac{\partial \phi}{\partial x} - \mu_p k_B T \frac{\partial p}{\partial x}, \quad (6)$$

respectively, where μ_s is a mobility of excitons, μ_n and μ_p represent mobilities of electrons and holes, respectively, k_B is a Boltzmann constant and T is a temperature. Here, we have assumed a validity of the Einstein relation ($D_{n,p,s}/\mu_{n,p,s} = k_B T/q$, where D_j , with $j \in \{n, p, s\}$, is a diffusion coefficient for electrons, holes and excitons, respectively). Similarly to other authors [26,30,32,33], we have decided to use the exciton mobility instead of the exciton diffusion coefficient.

A local electric potential ϕ can be found from the Poisson equation

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{q}{\epsilon_0 \epsilon_r} (p - n), \quad (7)$$

where ϵ_0 is a vacuum permittivity and ϵ_r represents a dielectric constant of material. Thus, an electric field can be calculated from the relation $E = -\partial\phi/\partial x$.

The bimolecular recombination rate R_B can be expressed as

$$R_B = \xi \gamma_L (np - n_{int}^2), \quad (8)$$

where ξ is a recombination reduction factor ($\xi \leq 1$), n_{int} represents the intrinsic carrier density in the bulk of material, and γ_L is a Langevin recombination coefficient, which is defined as

$$\gamma_L = \frac{q}{\epsilon_0 \epsilon_r} (\mu_n + \mu_p). \quad (9)$$

In order to determine the rate $k_{diss}(E)$, we assume that the dissociation of excitons into separated electrons and holes is described by the Onsager-Braun formalism [34,35]. Thus, the overall exciton dissociation probability can be expressed as [24,36]

$$D(E) = \int_0^\infty P(E, a) F(a) da, \quad (10)$$

where the probability of dissociation P for an exciton separation distance a is given by

$$P(E, a) = \frac{k_{diss}(E)}{k_{diss}(E) + k_f} \quad (11)$$

and F represents a normalized distribution function which is defined as [24,36]

$$F(a) = \frac{4}{\sqrt{\pi} a_0^3} a^2 \exp\left(-\frac{a^2}{a_0^2}\right). \quad (12)$$

In the above equations k_f is a decay rate of excitons ($k_f = 1/\tau_s$) and a_0 is an initial exciton separation distance.

The exciton dissociation rate can be expressed as

$$k_{diss}(E) = \frac{3q}{4\pi\epsilon_0\epsilon_r a^3} (\mu_n + \mu_p) \exp\left(-\frac{r}{a}\right) \frac{J_1(2\sqrt{-2b})}{\sqrt{-2b}}, \quad (13)$$

where J_1 is the first-order Bessel function, r is the Coulombic radius defined as

$$r = \frac{q^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (14)$$

and b is the electric field parameter given by

$$b = \frac{q^3 E}{8\pi\epsilon_0\epsilon_r k_B T^2}. \quad (15)$$

Boundary conditions for electric potential are taken as

$$\phi(0) = V_{built} - V_a, \quad \phi(L) = 0, \quad (16)$$

where V_{built} is a built-in voltage and V_a represents an applied voltage.

We assume that both electrodes form Schottky contacts. Therefore, the concentrations of electrons at both electrodes can be expressed as

$$n(0) = N_c \exp\left(\frac{-\phi_n}{k_B T}\right), \quad (17)$$

$$n(L) = N_c \exp\left(\frac{\phi_p - E_g}{k_B T}\right) \quad (18)$$

and boundary concentrations of holes are

$$p(0) = N_v \exp\left(\frac{\phi_n - E_g}{k_B T}\right), \quad (19)$$

$$p(L) = N_v \exp\left(\frac{-\phi_p}{k_B T}\right), \quad (20)$$

where L is a thickness of photoactive material, N_c and N_v are the effective densities of states in conduction and valence bands,

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